

Molecular Organization at Photo-responsive Surfaces formed by Self-Assembly

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Introduction: Semifluorinated side-chains attached to a polymer backbone can organize into well-ordered surface layers due to their combination of low surface energy and liquid crystallinity[1-2]. By introducing an azo group in the side chain we expect to be able to change the surface organization of these side chains irradiating the surface with UV light.

Methods and Materials: A new type of liquid crystalline side-chain, consisting of a fluoroazobenzene group (Fig. 1), was synthesized and attached to an isoprene block of a polystyrene-*b*-isoprene diblock copolymer. Water contact angles of the surface of these polymers were measured both before and immediately after UV irradiation. NEXAFS was used to probe the orientational behavior of the fluoroazobenzene side chains.

Results: The high contact angle values clearly show that these polymers have a highly hydrophobic surface. The longer -CF₂- helices have a higher contact angle, which indicates that these organize themselves to create a more uniform -CF₃ covered surface and make the surface more hydrophobic. The most interesting aspect of these polymers is that the contact angles decrease after 5 min. of UV irradiation. Our hypothesis is that the azo group in fluoroazobenzene side chain can undergo a *trans* to *cis* transition during UV exposure as shown in Fig. 2. The isomerization of the -N=N- just below the surface to the *cis* form, and the resulting disorientation of the -CF₂- helix, is expected to increase the polarity of the surface resulting in lower contact angles. The fact that such a transition occurs in bulk under our irradiation conditions can be verified by UV absorption measurements and is in agreement with results in the literature. After the UV source was turned off and the thin films were left in under white light for 10 minutes, the water contact angles were measured again. The results were same as the contact angles before UV exposure. This indicates that the side chains transform back from the *cis* to the *trans* conformation at the surface and that the effect of the UV irradiation of the surface is reversible, thus showing that the contact angle changes are not due to a chemical degradation of the surface by UV.

We have already measured the orientational parameters of the -CF₂- helix at room temperature of these polymers in the absence of UV irradiation. For example Fig. 3 shows the partial electron yield (PEY) spectrum of the surface of the fluoroazobenzene block copolymer F8. The spectrum shows that the PEY intensity from C 1s to σ^* of the C-F bonds increases with incident angle while that of C-C bonds decreases with incident angle. From the change of peak intensity with incident angle, we can calculate the orientational order parameters *S* for each bond and therefore the *S* and average tilt angles of -CF₂- helix axes. These results clearly show that the fluoroazobenzene side chains are well oriented toward the surface normal forming a -CF₃ surface, and that longer -CF₂- helices give rise to better orientation. The results for the F4, F6 and F8 also are in agreement with our hypothesis that decreases in water contact angle result from disorientation of the -CF₂- helices. The orientational order parameter and average tilt angle of phenyl rings, determined from the C 1s to π^* resonance, also are calculated. The normals to the phenyl rings are on average tilted 31° from surface normal.

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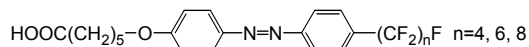


Fig. 1 The chemical structure of fluoroazobenzene side chains: F4(*n*=4); F6(*n*=6); F8(*n*=8).

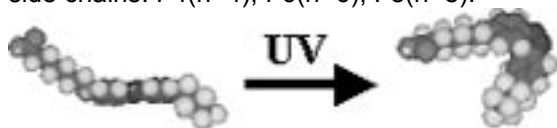


Fig. 2 The *trans*-to-*cis* transition of fluoroazobenzene side chains during UV exposure.

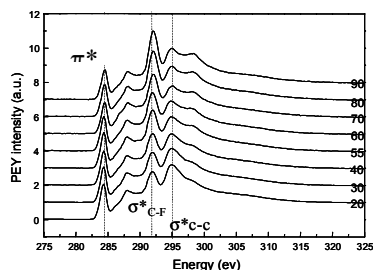


Fig. 3 The PEY spectrum of fluoroazobenzene block copolymer: F8.